TITLE:

Precipitation with Programmed Addition of Reagent-Precipitation of Manganese (II) : Oxinate in the Presence of Calcium and Magnesium

AUTHOR(S):

Fujinaga, Taitiro; Takagi, Osamu

CITATION:

Fujinaga, Taitiro ...[et al]. Precipitation with Programmed Addition of Reagent-Precipitation of Manganese (II) : Oxinate in the Presence of Calcium and Magnesium. Bulletin of the Institute for Chemical Research, Kyoto University 1976, 53(5): 460-463

ISSUE DATE:

1976-01-20

URL:

http://hdl.handle.net/2433/76635

RIGHT:

京都大学学術情報リポジトリ
KURENAI 紅
Kyoto University Research Information Repository

Bull. Inst. Chem. Res., Kyoto Univ., Vol. 53, No. 5, 1975

Precipitation with Programmed Addition of Reagent-Precipitation of Manganese (II) Oxinate in the Presence of Calcium and Magnesium

Taitiro FUJINAGA and Osamu TAKAGI

Received October 20, 1975

It is difficult to obtain pure Mn(II) oxinate precipitated in the presence of Ca and Mg. The authors have developed a new method of precipitation with programmed addition of reagent (PPAR method). In the present work, Mn(II) was quantitatively precipitated as the oxinate in the presence up to 50 mg of Mg by using the PPAR method. Similarly 25 mg of Mn(II) was determined in the presence of up to 100 mg of Ca. The results obtained by the present PPAR method were compared with those obtained by the conventional method and by the PFHS method.

INTRODUCTION

In spite of the big progress in the field of instrumental analysis, many reactions utilized for chemical analysis have not been controled with regard to the addition of reagents; usually a concentrated reagent solution is added by a pipet drop by drop to the sample solution. In this case, the precipitate is formed from a heterogeneous solution. On the other hand, Gordon developed a new method of precipitation from homogeneous solution (PFHS); first is added to the sample solution a reagent in the unreactive form which by heating transferred to the reactive form.

In the latter method, the rate of the reagent addition being necessary for precipitation is slower than the conventional method, but is not controled strictly.

The authors have developed a new method in which the rate of precipitation is programmed; the addition of reagent is automatically controled so as to raise pH at uniform rate. In the present paper, manganese(II) oxinate was precipitated in the presence of calcium and magnesium with the present method and the behaviors of the precipitate on the coprecipitation of Ca and Mg was investigated. The results were compared with those obtained with the conventional method and with the PFHS method.[1)]

EXPERIMENTAL

Reagents

Manganese(II) solution: A solution containing about 2.5 g Mn(II) per litre was prepared by dissolving $MnCl_2 \cdot 4H_2O$ in water. Mn(II) was standardized with EDTA solution which had been standardized with metallic zinc (99.999), Eriochrom Black T being used as indicator.

Urease: 0.05% aqueous solutions was prepared (activity 2250 Units per gram, Tokyo

* 藤永太一郎, 高木 修 : Department of Chemistry, Faculty of Science, Kyoto University, Kyoto.

Chemical Industry Co.), filtered and stored little by little in freezer and defrosted before use.

All chemicals used were analytical-reagent grade.

Apparatus

pH stat: Hiranuma Sangyo Co., Type Rat-101

pH meter: Hitachi-Horiba, Type M-5

Potentio-regulator: 10 turn 1 kΩ potentiometer connected with 20 kΩ rheostat in series and turned 10 times per 20 hours.

Procedure

Preparation of Smaple: To a splution containing exact 25.1 mg manganese(II) were added Ca or Mg, 100 mg of ascorbic acid, 1 ml of 1% citric acid solution and 10 ml of 2% ethanolic oxine solution. The solution was diluted to ca. 200 ml and pH was adjusted to 5.0 with ammonia solution. It was kept at 35°±0.1°C in a thermostat and the pH was monitored with a recorder.

1) *Conventional method*

To the solution prepared by the procedures mentioned above was added 0.1 N ammonia solution and raised pH within two minutes to the prescribed value. In increasing pH, care should be taken not to exceed the pH of the expected value by adding ammonia water drop by drop. The final pH of the solution was kept constant about 30 minutes by the pH stat.

2) *Programmed Precipitation method*

Setting was made by a rheostat; voltage was increased at a rate of 61.1 mV or 611 mV per hour. The voltage was supplied between the pH stat and a reference electrode (Fig. 1) by which the pH of the solution is raised linearly as is prescribed when ammonia

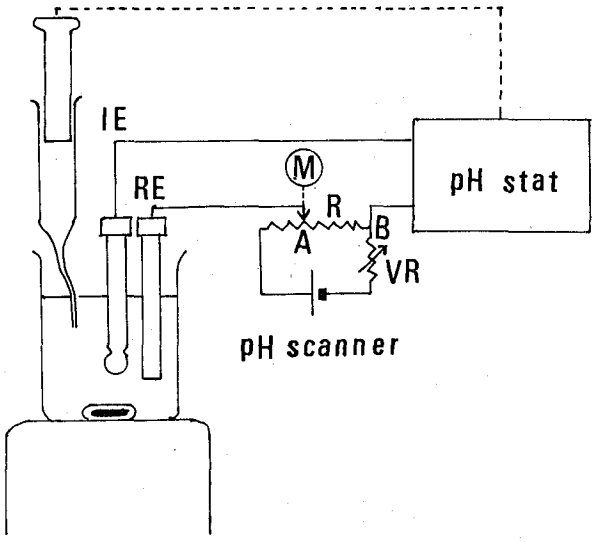

Fig. 1. Block Diagram of pH Programmer.

solution was added, the deviation of actual pH value from that of prescribed value was less than 0.05 in whole the range of pH examined. pH reaching to the prescribed value, regulator's motor was stopped and the solution was stirred 30 minutes at the final pH.

3) *PFHS method with urease*

To the solution was added 50 ml of 20% urea solution and 0.05% urease solution 2 ml. The precipitate was filtered off immediately in reaching to the prescribed pH.

Weighing of the Precipitate: In all the three methods, the precipitate filtered off with a glass filter 1G4, washed with warm water, dried 1 hour at 170°C and weighed.[2)]

Table I. Determination of Manganese (II) in the Presence of Mg

Mg 10 mg

pH	Conv (mg)	10 pH/hr (mg)	1 pH/hr (mg)	PFHS (mg)	Mn taken (mg)
7.0	27.1	26.2	25.9	25.6	25.1
6.5	26.1	25.4	25.1	24.6	25.1
6.0	25.6	25.0	25.1	20.5	25.1
5.5	24.2	24.8	24.7	17.9	25.1

Mg 50 mg

pH	Conc (mg)	10 pH/hr (mg)	1 PH/hr (mg)	PFHS (mg)	Mn taken (mg)
7.0	28.2	28.1	26.2	26.0	25.1
6.5	27.4	26.9	25.1	25.2	25.1
6.0	26.3	25.6	25.1	22.3	25.1
5.5	24.7	24.9	24.5	14.5	25.1

Table II. Determination of Manganese (II) in the Presence of Ca

Ca 50 mg

pH	Conv (mg)	10 pH/hr (mg)	1 pH/hr (mg)	PFHS (mg)	Mn taken (mg)
8.5	27.9	26.2	25.6	—	25.1
8.0	25.7	25.2	25.1	25.3	25.1
7.5	25.4	25.2	25.0	25.0	25.1
7.0	25.3	25.1	25.1	25.1	25.1
6.5	25.1	25.1	25.1	24.6	25.1

Ca 100 mg

pH	Conv (mg)	10 pH/hr (mg)	1 pH/hr (mg)	PFHS (mg)	Mn taken (mg)
8.5	29.4	27.0	26.2	—	25.1
8.0	26.2	25.4	25.1	25.3	25.1
7.5	25.9	25.3	25.1	25.0	25.1
7.0	25.2	25.2	25.1	25.1	25.1
6.5	25.1	25.1	25.0	24.6	25.1

RESULTS AND DISCUSSION

Mn(II) oxinate is precipitated quantitatively at pH over 6.[3] In the conventional method Mg was coprecipitated with Mn(II) oxinate over pH 6, so the determination of Mn(II) is impossible in the presence of much Mg. (Table I) By the programmed precipitation method, Mg was not coprecipitated in the presence of 50 mg Mg under the condition in raising pH 1 per hour indicating to the apparatus to keep pH under 6.5 automatically. Then it is possible to determine Mn(II) in the presence of Mg for the range of pH 6.0–6.5.

In the case of calcium, errors were not so gross in each method, especially increasing pH at a rate of 1 pH per hour Mn(II) was determined over the range of pH 6.0–8.0 in the presence of Ca 100 mg. (Table II)

With regard to the PFHS method by urease, the least pH of the quantitative precipitation of Mn(II) oxinate was higher than that of both the heterogeneous methods. On the other hand, in the presence of Mg at the pH 7.0 the oxinate began to coprecipitate. In the case of Ca, the least pH of the contamination was 8.0. Therefore, it is fairly difficult to determine Mn(II) separately in the presence of Mg or Ca by the PFHS method with urease.

REFERENCES

(1) S. Hikime, H. Yoshida, M. Taga, and S. Taguchi, *Talanta,* **19**, 569 (1972).
(2) S. Taguchi, M. Taga, H. Yoshida, and S. Hikime, *Japan Analyst,* **20**, 570 (1971).
(3) T. Tanaka and K. Hayashi, *Nippon Kagaku Kaishi*, **73**, 44 (1952).